

Kohn-Sham Theory in the Presence of Magnetic Field

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Abstract

In the well-known Kohn-Sham theory in Density Functional Theory, a fictitious non-interacting system is introduced that has the same particle density as a system of N electrons subjected to mutual Coulomb repulsion and an external electric field. For a long time, the treatment of the kinetic energy was not correct and the theory was not well-defined for N -representable particle densities. In the work of [Hadjisavvas and Theophilou, Phys. Rev. A, 1984, 30, 2183], a rigorous Kohn-Sham theory for N -representable particle densities was developed using the Levy-Lieb functional. Since a Levy-Lieb-type functional can be defined for Current Density Functional Theory formulated with the paramagnetic current density, we here develop a rigorous N -representable Kohn-Sham approach for interacting electrons in magnetic field. Furthermore, in the one-electron case, criteria for N -representable particle densities to be v -representable are given.

I. INTRODUCTION

In the fundamental paper by Hohenberg and Kohn [1], the theoretical foundation of Density Functional Theory (DFT) was established. The Hohenberg-Kohn theorem states that, for a quantum mechanical system, the particle density ρ determines the scalar potential of the system up to a constant. Subsequently, Kohn and Sham provided an algorithm [2], the so-called Kohn-Sham equations, for computing the density. These equations bear much resemblance to the Hartree-Fock integro-differential equations. The idea of Kohn and Sham was to introduce a fictitious system of non-interacting particles that has the same particle density as the real interacting system. This is achieved by means of the exchange-correlation functional, which accounts for the non-classical two-particle interactions and the residual between the interacting and non-interacting kinetic energy. However, this functional remains unknown.

In the work of Hadjisavvas and Theophilou [3], a mathematically rigorous Kohn-Sham approach was developed. The importance of this work relies on the fact that N -representability can be guaranteed for a proper wavefunction, whereas v -representability cannot. This means, in principle, that any v -representable formalism is unjustified.

In the presence of a magnetic field, no Hohenberg-Kohn theorem exists at the present time (that is valid for any number of electrons). For the formulation of Current Density Functional Theory (CDFT) that uses the paramagnetic current density j^p , it is well-known that the density pair (ρ, j^p) does not determine the scalar potential and vector potential of the system [4]. Counterexamples have been constructed that show that a ground-state can come from two different Hamiltonians [4, 5]. Thus, the particle density ρ and the paramagnetic current density j^p do not fully determine the Hamiltonian. For a many-electron system, neither proof nor counterexample exists so far in the literature for a Hohenberg-Kohn theorem formulated with the total current density j [5, 6]. In the one-electron case, on the other hand, it is possible to give a direct proof that ρ and j determine the scalar and vector potential up to a gauge transformation [5, 6].

However, since the density pair (ρ, j^p) determines the (possibly degenerate) ground-state(s) of the system [5, 7], this work aims at continue the N -representable approach of [3] and develop a rigorous Kohn-Sham approach for CDFT formulated with the paramagnetic current density j^p .

II. CURRENT DENSITY FUNCTIONAL THEORY

We will in this paper consider a system of N interacting electrons subjected to both an electric and a magnetic field. The system's Hamiltonian is given by (in suitable units)

$$H(v, A) = \sum_{k=1}^N \left((i\nabla_k - A(x_k))^2 + v(x_k) \right) + \sum_{1 \leq k < l \leq N} |x_k - x_l|^{-1},$$

where $v(x)$ is the scalar potential and $A(x)$ the vector potential. The magnetic field is computed from $B(x) = \nabla \times A(x)$. Throughout we will assume that the ground-state is non-degenerate, i.e., $\dim \ker(e_0 - H(v, A)) = 1$, where e_0 is the lowest eigenvalue of $H(v, A)$.

A. Preliminaries

To begin with, some mathematical concepts needed for the forthcoming discussion are introduced. We first mention some relevant function spaces. If for some $p \in [1, \infty)$ a function f satisfies $\int_{\mathbb{R}^n} |f|^p < \infty$, then f belongs to the normed space $L^p(\mathbb{R}^n)$ with norm $\|f\|_{L^p(\mathbb{R}^n)} = (\int_{\mathbb{R}^n} |f|^p)^{1/p}$. In the case $p = \infty$, we say $f \in L^\infty(\mathbb{R}^n)$ if

$$\|f\|_{L^\infty(\mathbb{R}^n)} = \text{ess sup}\{|f| \mid x \in \mathbb{R}^n\} < \infty.$$

Furthermore, $f \in L^2(\mathbb{R}^n)$ is said to belong to the Hilbert space $\mathcal{H}^1(\mathbb{R}^n)$ if

$$\|f\|_{\mathcal{H}^1(\mathbb{R}^n)}^2 = \int_{\mathbb{R}^n} |f|^2 + \int_{\mathbb{R}^n} |\nabla f|^2 < \infty.$$

Let $B_R = \{x \in \mathbb{R}^n \mid |x| \leq R\}$ for $R > 0$. Then $f \in L^1_{\text{loc}}(\mathbb{R}^n)$ whenever $\int_{B_R} |f| < \infty$ for any B_R . For a vector u such that $(u)_l \in L^p$, $l = 1, 2, 3$, we write $u \in (L^p)^3$.

We say that a sequence $\{\psi_k\} \subset L^p(\mathbb{R}^n)$ converges in $L^p(\mathbb{R}^n)$ -norm to $\psi \in L^p(\mathbb{R}^n)$ if $\int_{\mathbb{R}^n} |\psi_k - \psi|^p \rightarrow 0$ as $k \rightarrow \infty$, and we write $\psi_k \rightarrow \psi$. For the Hilbert space $L^2(\mathbb{R}^n)$, with inner product $(\psi, \phi)_{L^2(\mathbb{R}^n)} = \int_{\mathbb{R}^n} \psi^* \phi$, we say that $\{\psi_k\} \subset L^2(\mathbb{R}^n)$ converges weakly to $\psi \in L^2(\mathbb{R}^n)$ if $(\psi_k, \phi)_{L^2(\mathbb{R}^n)} \rightarrow (\psi, \phi)_{L^2(\mathbb{R}^n)}$ as $k \rightarrow \infty$ for all $\phi \in L^2(\mathbb{R}^n)$, and we write $\psi_k \rightharpoonup \psi$. For weak convergence in $\mathcal{H}^1(\mathbb{R}^n)$, we require $(\psi_k, \phi)_{\mathcal{H}^1(\mathbb{R}^n)} \rightarrow (\psi, \phi)_{\mathcal{H}^1(\mathbb{R}^n)}$ as $k \rightarrow \infty$ for all $\phi \in \mathcal{H}^1(\mathbb{R}^n)$, where the inner product of $\mathcal{H}^1(\mathbb{R}^n)$ is given by $(\psi, \phi)_{\mathcal{H}^1(\mathbb{R}^n)} = \int_{\mathbb{R}^n} \psi^* \phi + \int_{\mathbb{R}^n} \nabla \psi^* \cdot \nabla \phi$. Weak convergence on $\mathcal{H}^1(\mathbb{R}^n)$ implies weak convergence in the $L^2(\mathbb{R}^n)$ sense. A functional f is said to be weakly lower semi continuous if $\psi_k \rightharpoonup \psi$ implies $\liminf_{k \rightarrow \infty} f(\psi_k) \geq f(\psi)$. In particular, $\liminf_{k \rightarrow \infty} \|\psi_k\|_{L^2(\mathbb{R}^n)} \geq \|\psi\|_{L^2(\mathbb{R}^n)}$ if $\psi_k \rightharpoonup \psi$ weakly in $L^2(\mathbb{R}^n)$.

For a fixed particle number N , define the set of proper wavefunctions to be

$$W_N = \{\psi \in \mathcal{H}^1(\mathbb{R}^{3N}) | \psi \text{ antisymmetric and } \|\psi\|_{L^2(\mathbb{R}^{3N})} = 1\}$$

and let the ground-state energy of $H(v, A)$ be given by

$$e_0(v, A) = \inf\{\mathcal{E}_{v,A}(\psi) | \psi \in W_N\},$$

where

$$\mathcal{E}_{v,A}(\psi) = \sum_{k=1}^N \left(\int_{\mathbb{R}^{3N}} |(i\nabla_k - A(x_k))\psi|^2 + \int_{\mathbb{R}^{3N}} |\psi|^2 v(x_k) \right) + \sum_{1 \leq k < l \leq N} \int_{\mathbb{R}^{3N}} |\psi|^2 |x_k - x_l|^{-1}.$$

We will define the inner-product $(\psi, H(v, A)\psi)_{L^2}$ as the number $\mathcal{E}_{v,A}(\psi)$ for $\psi \in W_N$, even if $H(v, A)\psi \notin L^2$.

The particle and paramagnetic current density for $\psi \in W_N$ are computed from

$$\begin{aligned} \rho_\psi(x) &= N \int_{\mathbb{R}^{3(N-1)}} |\psi(x, x_2, \dots, x_N)|^2 dx_2 \dots dx_N, \\ j_\psi^p(x) &= N \operatorname{Im} \int_{\mathbb{R}^{3(N-1)}} \psi^*(x, x_2, \dots, x_N) \nabla_x \psi(x, x_2, \dots, x_N) dx_2 \dots dx_N, \end{aligned}$$

respectively. We will use the notation $\psi \mapsto (\rho, j^p)$ to mean $\rho_\psi = \rho$ and $j_\psi^p = j^p$. Furthermore, we shall use the notation H_0 for the Hamiltonian $H(v, A)$ when the potential terms are set to zero, i.e.,

$$(\psi, H_0\psi)_{L^2} = \sum_{k=1}^N \int_{\mathbb{R}^{3N}} |\nabla_k \psi|^2 + \sum_{1 \leq k < l \leq N} \int_{\mathbb{R}^{3N}} |\psi|^2 |x_k - x_l|^{-1}.$$

Note that

$$\mathcal{E}_{v,A}(\psi) = (\psi, H(v, A)\psi)_{L^2} = (\psi, H_0\psi)_{L^2} + 2 \int_{\mathbb{R}^3} j_\psi^p \cdot A + \int_{\mathbb{R}^3} \rho_\psi (v + |A|^2),$$

which follows from a direct computation.

B. N -representable DFT

A v -representable particle density is a density ρ that satisfies $\rho = \rho_\psi$ and where ψ is the ground-state of some $H(v)$. (We will use the notation $H(v) = H(v, 0)$ and $e_0(v) = e_0(v, 0)$ when not considering magnetic fields.) The set of N -representable particle densities is given by [8]

$$I_N = \left\{ \rho | \rho \geq 0, \int_{\mathbb{R}^3} \rho = N, \rho^{1/2} \in \mathcal{H}^1(\mathbb{R}^3) \right\}.$$

As demonstrated by Englisch and Englisch in [9], not every N -representable particle density is v -representable. For $\rho \in I_N$, the Levy-Lieb functional

$$F_{LL}(\rho) = \inf\{(\psi, H_0\psi)_{L^2} | \psi \in W_N, \psi \mapsto \rho\}$$

is well-defined. As was proven in [8] (Theorem 3.3), there exists a $\psi_0 \in W_N$ such that $F_{LL}(\rho) = (\psi_0, H_0\psi_0)_{L^2}$ and $\rho_{\psi_0} = \rho$. The functional $F_{LL}(\rho)$ extends the Hohenberg-Kohn functional to N -representable densities, and for the ground-state energy we have

$$e_0(v) = \inf \left\{ F_{LL}(\rho) + \int_{\mathbb{R}^3} \rho v | \rho \in I_N \right\}.$$

Note that the number $e_0(v)$ is well-defined for $v \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ even if $H(v)$ does not have a ground-state. ($\int_{\mathbb{R}^3} \rho v$ is finite for all $\rho \in I_N$, since $I_N \subset L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$, see [8].)

C. N -representable CDFT

A density pair (ρ, j^p) is said to be v -representable if there exists a ψ that is the ground-state of some Hamiltonian $H(v, A)$ such that $\rho = \rho_\psi$ and $j^p = j_\psi^p$. We denote this set of densities \mathcal{A}_N , i.e.,

$$\mathcal{A}_N = \{(\rho, j^p) | \text{there exists a } H(v, A) \text{ with ground-state } \psi \text{ such that } \psi \mapsto (\rho, j^p)\}.$$

Now, assume that $H(v_1, A_1)$ and $H(v_2, A_2)$ have the ground-states ψ and ϕ , respectively. Then from Theorem 9 in [5], if $\psi \mapsto (\rho, j^p)$ and $\phi \mapsto (\rho, j^p)$, it follows that $\psi = \text{const. } \phi$. For $(\rho, j^p) \in \mathcal{A}_N$, let ψ_{ρ, j^p} denote the ground-state of some $H(v, A)$ such that $\psi \mapsto (\rho, j^p)$. Then the generalized Hohenberg-Kohn functional

$$F_{HK}(\rho, j^p) = (\psi_{\rho, j^p}, H_0\psi_{\rho, j^p})_{L^2}$$

is well-defined on \mathcal{A}_N . Furthermore (Theorem 2 in [10]),

$$e_0(v, A) = \min \left\{ F_{HK}(\rho, j^p) + 2 \int_{\mathbb{R}^3} j^p \cdot A + \int_{\mathbb{R}^3} \rho(v + |A|^2) \middle| (\rho, j^p) \in \mathcal{A}_N \right\}$$

for $(v, A) \in V_N$, where

$$V_N = \{(v, A) | H(v, A) \text{ has a unique ground-state}\}.$$

However, a $\psi \in W_N$ may be such that $(\rho_\psi, j_\psi^p) \notin \mathcal{A}_N$. From Proposition 3 in [10], $\psi \in W_N$ implies that $\psi \mapsto (\rho, j^p) \in Y_N$, where

$$Y_N = \left\{ (\rho, j^p) \mid \rho \geq 0, \int_{\mathbb{R}^3} \rho = N, \rho^{1/2} \in \mathcal{H}^1(\mathbb{R}^3), j^p \in (L^1(\mathbb{R}^3))^3, \int_{\mathbb{R}^3} |j^p|^2 \rho^{-1} < \infty \right\}.$$

The set Y_N is referred to as the set of N -representable density pairs (ρ, j^p) . It is a convex set and $\mathcal{A}_N \subsetneq Y_N$ (Proposition 4 in [10]). For $(\rho, j^p) \in Y_N$, define as in [10]

$$Q(\rho, j^p) = \inf \{ (\psi, H_0 \psi)_{L^2} \mid \psi \in W_N, \psi \mapsto (\rho, j^p) \}.$$

The functional $Q(\rho, j^p)$ is the generalization of the Levy-Lieb functional $F_{LL}(\rho)$. It also depends on the paramagnetic current density j^p . The functional $Q(\rho, j^p)$ inherits many properties of $F_{LL}(\rho)$: by Theorem 5 and Theorem 6 in [10], we have (i) $Q(\rho, j^p) = F_{HK}(\rho, j^p)$ for $(\rho, j^p) \in \mathcal{A}_N$, (ii) there exists a $\psi_m \in W_N$ such that $Q(\rho, j^p) = (\psi_m, H_0 \psi_m)_{L^2}$ and where $\psi_m \mapsto (\rho, j^p)$, and (iii)

$$e_0(v, A) = \inf \left\{ Q(\rho, j^p) + 2 \int_{\mathbb{R}^3} j^p \cdot A + \int_{\mathbb{R}^3} \rho(v + |A|^2) \mid (\rho, j^p) \in Y_N \right\}.$$

In [3], $F_{LL}(\rho)$ was used to obtain a rigorous Kohn-Sham theory for N -representable densities. Before generalizing this to CDFT formulated with j^p , we shall discuss the following question raised in [3]: since a $\psi_0 \in W_N$ exists such that $F_{LL}(\rho) = (\psi_0, H_0 \psi_0)_{L^2}$ and $\psi_0 \mapsto \rho$, does ψ_0 satisfy any Schrödinger equation, i.e., is there a $v(x)$ such that $H(v)\psi = e\psi$?

III. CHARACTERIZATION OF V -REPRESENTABLE PARTICLE DENSITIES

We start by stating the mentioned result of Lieb (Theorem 3.3 in [8]) for the functional $F_{LL}(\rho)$.

Theorem 1 *There exists a ψ_0 in W_N such that for $\rho \in I_N$, $F_{LL}(\rho) = (\psi_0, H_0 \psi_0)_{L^2}$ and $\rho_{\psi_0} = \rho$.*

Let $\rho \in I_N$. In light of Theorem 1, if the minimizer ψ_0 would be the ground-state of some Hamiltonian $H(v)$, then ρ would be v -representable. However, since the v -representable densities are a proper subset of the N -representable ones [9], there exists $\rho \in I_N$ such that the corresponding minimizer ψ_0 is not the ground-state of any Hamiltonian $H(v)$. Also note

that, if ρ is v -representable, then the minimizer ψ_0 is also the ground-state associated with ρ . This so since if ρ is v -representable, then by the definition of the minimizer ψ_0 , we have

$$(\psi_0, H_0\psi_0)_{L^2} + \int_{\mathbb{R}^3} \rho v = e_0(v)$$

for some v , i.e., ψ_0 is the ground-state of $H(v)$. (A similar result holds for a minimizer of $Q(\rho, j^p)$, see Proposition 5.)

Now, let $N = 1$. Note the following: $(\psi, H_0\psi)_{L^2} = \int_{\mathbb{R}^3} |\nabla\psi|^2 dx \geq \int_{\mathbb{R}^3} |\nabla|\psi||^2 dx$. Thus, for $F_{LL}(\rho)$, it is enough to minimize over the non-negative functions of W_1 , i.e.,

$$F_{LL}(\rho) = \inf \left\{ \int_{\mathbb{R}^3} |\nabla\psi|^2 dx \mid \psi \in W_1, \psi \geq 0, \psi^2 = \rho \right\}.$$

We now give criteria when ψ_0 in Theorem 1 is an eigenfunction of some $H(v)$.

Proposition 2 (i) Let $N = 1$ and $\rho \in I_1$ be such that ψ_0 fulfills $\Delta\psi_0 \in L^2(\mathbb{R}^3)$ and $\psi_0 \neq 0$ almost everywhere (a.e.), where $\psi_0 \geq 0$ minimizes $\int_{\mathbb{R}^3} |\nabla\psi|^2$ subject to the constraint $\psi^2 = \rho$. Then there exists a $\phi_0 \in L^2(\mathbb{R}^3)$ and a constant e such that, with $v - e = \phi_0/\rho^{1/2}$, ψ_0 satisfies

$$-\Delta\psi_0 + v\psi_0 = e\psi_0,$$

and where $\int_{\mathbb{R}^3} v|\psi_0|^2 > -\infty$.

(ii) For $N = 1$, there exists $\rho_0 \in I_1$ such that $\Delta\psi_0 \notin L^2(\mathbb{R}^3)$, and $-\Delta\psi_0 + v\psi_0 = 0$ implies $\int_{\mathbb{R}^3} v|\psi_0|^2 = -\infty$.

Proof. By assumption, $\psi_0 > 0$ a.e. and $\psi_0 = \rho^{1/2}$. Now, set $\phi_0 = \Delta\psi_0$, which is in $L^2(\mathbb{R}^3)$. Then with $v - e = \phi_0/\rho^{1/2}$ the conclusion of the first part follows, since

$$\int_{\mathbb{R}^3} v|\psi_0|^2 = \int_{\mathbb{R}^3} \phi_0 \rho^{1/2} + e \geq -\|\phi_0\|_{L^2} + e.$$

For the second part, set, for small $|x_1|$, $\rho_0(x) = \rho_1(x_1)\tilde{\rho}(x_2, x_3)$, where $\tilde{\rho}(x_2, x_3)$ is regular and $\rho_1(x_1) = (a + b|x_1|^{\varepsilon+1/2})^2$, $a, b < 0$ and $0 < \varepsilon < 1/2$. Then $\Delta\psi_0 \notin L^2(\mathbb{R}^3)$. Furthermore, $-\Delta\psi_0 + v\psi_0 = 0$ implies $\int_{\mathbb{R}^3} v|\psi_0|^2 = -\infty$. (The density ρ_0 is the counterexample of Englisch and Englisch that shows that not every N -representable density is v -representable, see [9].) ■

Note that ψ_0 is not proven to be the ground-state of $-\Delta + v$. However, we have

Corollary 3 *Let ρ , ψ_0 and ϕ_0 be as in Proposition 2 (i). In addition, assume that $\phi_0 \leq C\rho^{1/2}$ for some constant C and that $\rho^{-1} \in L^1_{\text{loc}}(\mathbb{R}^3)$. Then ψ_0 is the ground-state of $-\Delta + v$.*

Proof. From Proposition 2, we know that $-\Delta\psi_0 + v\psi_0 = e\psi_0$, where $v = \phi_0/\rho^{1/2} + e$. By Schwarz's inequality, it follows that $v \in L^1_{\text{loc}}(\mathbb{R}^3)$. Since v is also bounded above, we have by Corollary 11.9 in [11] that $\psi_0 > 0$ is the ground-state of $-\Delta + v$. ■

We can thus conclude with the following characterization: if $\rho \in I_1$ satisfies (i) $\rho > 0$ (a.e.), (ii) $\Delta\rho^{1/2} \in L^2(\mathbb{R}^3)$ and bounded above by a constant times $\rho^{1/2}$, and (iii) $\rho^{-1} \in L^1_{\text{loc}}$, then ρ is v -representable.

IV. RIGOROUS KOHN-SHAM THEORY FOR CDFT

By means of the Levy-Lieb-type density functional $Q(\rho, j^p)$ we can formulate a rigorous N -representable Kohn-Sham approach for CDFT as that of Ref. [3] for DFT. Now, fix the particle number N . We say that a wavefunction $\phi \in W_N$ is a determinant if there exist N orthonormal one-particle functions f_k such that

$$\phi(x_1, \dots, x_N) = (N!)^{-1/2} \det[f^k(x_l)]_{k,l}.$$

Let the space of all normalized determinants of finite kinetic energy be denoted W_S , i.e.,

$$W_S = \{\phi | \phi \text{ is a determinant, } \|\phi\|_{L^2(\mathbb{R}^{3N})} = 1, (\phi, K\phi)_{L^2(\mathbb{R}^{3N})} < \infty\},$$

where $K = -\sum_{k=1}^N \Delta_k$. Note that, in particular, for a $\phi \in W_S$, we have $\rho_\phi = \sum_{k=1}^N |f^k|^2$ and

$$(\phi, K\phi)_{L^2(\mathbb{R}^{3N})} = \sum_{k=1}^N \int_{\mathbb{R}^3} |\nabla f^k|^2 dx.$$

Thus, $\|\phi\|_{L^2(\mathbb{R}^{3N})} = 1$ and $(\phi, K\phi)_{L^2(\mathbb{R}^{3N})} < \infty$ are equivalent to $f^k \in \mathcal{H}^1(\mathbb{R}^3)$ for all k . Also note that a $\psi \in W_N$ is not in general an element of W_S , i.e., $W_S \subsetneq W_N$.

Furthermore, define, for a non-interacting system, the non-interacting Hamiltonian

$$H'(v, A) = \sum_{k=1}^N ((i\nabla_k - A(x_k))^2 + v(x_k)).$$

The non-interacting ground-state energy is then given by

$$e'_0(v, A) = \inf\{\mathcal{E}'_{v,A}(\psi) | \psi \in W_N\},$$

where $\mathcal{E}'_{v,A}(\psi)$ is given by the relation

$$\mathcal{E}'_{v,A}(\psi) + \sum_{1 \leq k < l \leq N} \int_{\mathbb{R}^{3N}} |\psi|^2 |x_k - x_l|^{-1} = \mathcal{E}_{v,A}(\psi).$$

This motivates: set, for $(\rho, j^p) \in Y_N$,

$$Q'(\rho, j^p) = \inf\{(\psi, K\psi)_{L^2} | \psi \in W_N, \psi \mapsto (\rho, j^p)\}.$$

For $Q(\rho, j^p)$ and $Q'(\rho, j^p)$ we have the following.

Theorem 4 *Fix $(\rho, j^p) \in Y_N$, then (i) there exists a $\psi_m \in W_N$ such that $\psi_m \mapsto (\rho, j^p)$ and $Q(\rho, j^p) = (\psi_m, H_0 \psi_m)_{L^2}$, and (ii) there exists a $\psi'_m \in W_N$ such that $\psi'_m \mapsto (\rho, j^p)$ and $Q'(\rho, j^p) = (\psi'_m, K \psi'_m)_{L^2}$.*

Proof. Part (i) above is just Theorem 5 in [10]. However, for (ii), we can use the same proof. For the sake of completeness we include the proof in [10] here applied to $Q'(\rho, j^p)$.

Let $\{\psi^j\}_{j=1}^\infty$ be a minimizing sequence, i.e., $\psi^j \in W_N$, $\psi^j \mapsto (\rho, j^p)$ and

$$\lim_{j \rightarrow \infty} (\psi^j, K \psi^j)_{L^2} = Q'(\rho, j^p).$$

Since $\{\psi^j\}_{j=1}^\infty$ is bounded in $\mathcal{H}^1(\mathbb{R}^{3N})$, by the Banach-Alaoglu theorem there exists a subsequence and a $\psi'_m \in \mathcal{H}^1(\mathbb{R}^{3N})$ such that $\psi^{j_k} \rightharpoonup \psi'_m$ weakly in $\mathcal{H}^1(\mathbb{R}^{3N})$ as $k \rightarrow \infty$. Since the functional $\psi \mapsto (\psi, K \psi)_{L^2}$ is weakly lower semi continuous, we know that

$$(\psi'_m, K \psi'_m)_{L^2} \leq Q'(\rho, j^p).$$

However, it remains to prove that $\psi'_m \mapsto (\rho, j^p)$. In the proof of Theorem 3.3 in [8], it is shown that $\psi^{j_k} \rightarrow \psi'_m$ in $L^2(\mathbb{R}^{3N})$ and $\psi'_m \mapsto \rho$. Now, let g be the characteristic function of any measurable set in \mathbb{R}^3 . For $l = 1, 2, 3$ and $k = 1, 2, \dots$, let

$$I_l(k) = \left| \int_{\mathbb{R}^{3N}} [(\psi^{j_k})^* \partial_l \psi^{j_k} - (\psi'_m)^* \partial_l \psi'_m] g \right|.$$

Then

$$\begin{aligned} I_l(k) &\leq \left| \int_{\mathbb{R}^{3N}} (\psi^{j_k} - \psi'_m)^* (\partial_l \psi^{j_k}) g \right| + \left| \int_{\mathbb{R}^{3N}} (\psi'_m)^* (\partial_l \psi^{j_k} - \partial_l \psi'_m) g \right| \\ &\leq \|\psi^{j_k} - \psi'_m\|_{L^2} \|(\partial_l \psi^{j_k}) g\|_{L^2} + \left| \int_{\mathbb{R}^{3N}} (\psi'_m g^*)^* (\partial_l \psi^{j_k} - \partial_l \psi'_m) \right|. \end{aligned}$$

Thus $I_l(k)$ tends to zero as $k \rightarrow \infty$ (because $\psi^{j_k} \rightarrow \psi'_m$ in $L^2(\mathbb{R}^{3N})$ -norm and $\psi^{j_k} \rightharpoonup \psi'_m$ weakly in $\mathcal{H}^1(\mathbb{R}^{3N})$ as $k \rightarrow \infty$). Since $\psi^{j_k} \mapsto j^p$ for all k , we have $\int_{\mathbb{R}^3} (j^p)_l g = \int_{\mathbb{R}^3} (j_{\psi'_m}^p)_l g$, i.e., $j_{\psi'_m}^p(x) = j^p(x)$ a.e. \blacksquare

Proposition 5 Assume that $(\rho, j^p) \in \mathcal{A}_N$, i.e., there exists a $H(v, A)$ with ground-state ψ such that $\psi \mapsto (\rho, j^p)$. Then the minimizer ψ_m is the ground-state of $H(v, A)$.

Proof. Since $\psi \mapsto (\rho, j^p)$, we have $(\psi, H_0\psi)_{L^2} \geq (\psi_m, H_0\psi_m)_{L^2}$. The conclusion then follows from

$$\begin{aligned} e_0(v, A) &\leq (\psi_m, H(v, A)\psi_m)_{L^2} = (\psi_m, H_0\psi_m)_{L^2} + 2 \int_{\mathbb{R}^3} j^p \cdot A + \int_{\mathbb{R}^3} \rho(v + |A|^2) \\ &\leq (\psi, H_0\psi)_{L^2} + 2 \int_{\mathbb{R}^3} j^p \cdot A + \int_{\mathbb{R}^3} \rho(v + |A|^2) = (\psi, H(v, A)\psi)_{L^2} = e_0(v, A). \blacksquare \end{aligned}$$

Note that when H_0 is replaced by K , $Q'(\rho, j^p)$ is the minimal kinetic energy for $\psi \in W_N$ such that $\rho_\psi = \rho$ and $j_\psi^p = j^p$. Next we will introduce another kinetic energy density functional.

A. Non-interacting kinetic energy density functional

Set, for $(\rho, j^p) \in Y_N$,

$$T_{\det}(\rho, j^p) = \inf\{(\phi, K\phi)_{L^2} \mid \phi \in W_S, \phi \mapsto (\rho, j^p)\}.$$

For $(\rho, j^p) \in Y_N$, we remark that the set $\{\phi \in W_S \mid \phi \mapsto (\rho, j^p)\}$ is not empty, at least when $N \geq 4$. This follows from the determinant construction in [12]. However, for all N , the set $\{\phi \in W_S \mid \phi \mapsto (\rho, j^p), \nabla \times (j^p/\rho) = 0\}$ is non-empty (see [10, 12]).

We have that $T_{\det}(\rho, j^p) \geq Q'(\rho, j^p)$ on Y_N . Now, let the set of non-interacting v -representable densities be denoted \mathcal{A}'_N ,

$$\mathcal{A}'_N = \{(\rho, j^p) \mid H'(v, A) \text{ has a unique ground-state}\}.$$

If $(\rho, j^p) \in \mathcal{A}'_N$, by the same argument as in the proof of Proposition 5, we can conclude that ψ'_m is the ground-state of some $H'(v, A)$. Clearly, ψ'_m is in this case a determinant. Thus, $T_{\det}(\rho, j^p) = Q'(\rho, j^p)$ on \mathcal{A}'_N .

An important property of $T_{\det}(\rho, j^p)$ is that the infimum actually is a minimum. For the proof, we need the following:

(i) For $k = 1, \dots, N$, assume that $f_j^k \rightarrow f^k$ in L^2 -norm as $j \rightarrow \infty$ and for each j , $(f_j^k, f_j^l)_{L^2} = \delta_{kl}$. Then f^1, \dots, f^N are orthonormal. This so since

$$(f^k, f^l)_{L^2} = \lim_{j \rightarrow \infty} (f_j^k, f_j^l)_{L^2} = \lim_{j \rightarrow \infty} [(f_j^k, f_j^l - f_j^l)_{L^2} + (f_j^k, f_j^l)_{L^2}] = \delta_{kl},$$

where we used that $|(f_j^k, f^l - f_j^l)_{L^2}| \leq \|f_j^k\|_{L^2} \|f^l - f_j^l\|_{L^2} \rightarrow 0$ as $j \rightarrow \infty$.

(ii) If $f_j \rightharpoonup f$ weakly in L^2 as $j \rightarrow \infty$ and $\|f_j\|_{L^2} \rightarrow \|f\|_{L^2}$ as $j \rightarrow \infty$, then $f_j \rightarrow f$ in L^2 -norm as $j \rightarrow \infty$. (This is an elementary fact and can be checked by expanding $\|f_j - f\|_{L^2}^2 = (f_j - f, f_j - f)_{L^2}$.)

Theorem 6 *Let $(\rho, j^p) \in Y_N$. If $N < 4$ we also assume $\nabla \times (j^p/\rho) = 0$. Then there exists a determinant ϕ_m such that $\phi_m \mapsto (\rho, j^p)$ and $T_{\det}(\rho, j^p) = (\phi_m, K\phi_m)_{L^2}$.*

Proof. Fix $(\rho, j^p) \in Y_N$ and let $\{D^j\}_{j=1}^\infty \subset W_S$ be a sequence of minimizing determinants, i.e., $D^j \mapsto (\rho, j^p)$ and $\lim_{j \rightarrow \infty} (D^j, KD^j)_{L^2} = T_{\det}(\rho, j^p)$. From the proof of Theorem 4, there exists a subsequence D^{j_n} and a $\phi_m \in W_N$ such that $\phi_m \mapsto (\rho, j^p)$,

$$T_{\det}(\rho, j^p) = (\phi_m, K\phi_m)_{L^2}$$

and $D^{j_n} \rightarrow \phi_m$ in L^2 -norm. It remains to show that $\phi_m \in W_S$. To meet that end, let

$$D^j(x_1, \dots, x_N) = (N!)^{-1/2} \det[f_j^k(x_l)]_{k,l},$$

where for each j the N one-particle functions f_j^k are orthonormal. By the Banach-Alaoglu theorem, there exist N functions f^k such that (for a subsequence) $f_j^k \rightharpoonup f^k$ weakly in L^2 as $j \rightarrow \infty$. We furthermore claim that f^1, \dots, f^N are orthonormal. If we could prove that $f_j^k \rightarrow f^k$ in L^2 -norm, it would follow that $(f^k, f^l)_{L^2} = \delta_{kl}$.

We shall prove $f_j^k \rightarrow f^k$ by demonstrating that $\|f_j^k\|_{L^2} \rightarrow \|f^k\|_{L^2}$. This together with the fact that $f_j^k \rightharpoonup f^k$ weakly in L^2 gives the desired result. Let $\varepsilon > 0$ and choose a characteristic function χ such that $\int_{\mathbb{R}^3} \rho(1 - \chi) < \varepsilon$. Since for each j , $D^j \mapsto \rho$, we have for each k ,

$$\int_{\mathbb{R}^3} |f_j^k|^2 (1 - \chi) \leq \sum_{k=1}^N \int_{\mathbb{R}^3} |f_j^k|^2 (1 - \chi) = \int_{\mathbb{R}^3} \rho(1 - \chi) < \varepsilon.$$

By the Rellich-Kondrachov theorem, we can choose a subsequence such that $\chi f_{j_n}^k \rightarrow \chi f^k$ in L^2 -norm. But this implies

$$\int_{\mathbb{R}^3} |f^k|^2 \geq \int_{\mathbb{R}^3} \chi |f^k|^2 = \lim_{n \rightarrow \infty} \int_{\mathbb{R}^3} \chi |f_{j_n}^k|^2 \geq 1 - \varepsilon.$$

Conversely, by the lower semi continuity of the L^2 -norm, $1 = \liminf_{j \rightarrow \infty} \|f_j^k\|_{L^2} \geq \|f^k\|_{L^2}$, and we have $\|f^k\|_{L^2} = 1$.

Returning to the fact that $f_{j_n}^k \rightharpoonup f^k$ weakly in L^2 , we note that $\Pi_{k=1}^N f_{j_n}^k(x_k) \rightharpoonup \Pi_{k=1}^N f^k(x_k)$ weakly in $L^2(\mathbb{R}^{3N})$ (since product-functions are dense in $L^2(\mathbb{R}^{3N})$). But then

$$D^{j_n} \rightharpoonup (N!)^{-1/2} \det[f^k(x_l)]_{k,l},$$

where f^1, \dots, f^N are orthonormal. However, since $D^{j_n} \rightarrow \phi_m$, we have $\phi_m \in W_S$. \blacksquare

B. N -representable Kohn-Sham theory

In the Kohn-Sham approach [2], a non-interacting system is introduced that has the same ground-state density as the fully interacting system. The idea is then to use an element of W_S , i.e., a determinant, to compute the ground-state density. On \mathcal{A}'_N , the (generalized) Kohn-Sham density functional $T_{KS}(\rho, j^p)$ satisfies

$$T_{KS}(\rho, j^p) = T_{\det}(\rho, j^p) = Q'(\rho, j^p).$$

Moreover, T_{KS} defines an exchange-correlation functional $E_{xc}(\rho, j^p)$ on $\mathcal{A}_N \cap \mathcal{A}'_N$ according to

$$E_{xc}(\rho, j^p) = F_{HK}(\rho, j^p) - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dx dy - T_{KS}(\rho, j^p).$$

Now, to obtain an N -representable Kohn-Sham scheme, define two functionals on W_S ,

$$\mathcal{G}_K(\phi) = \inf\{(f, Kf)_{L^2} | f \in W_S, f \mapsto (\rho_\phi, j_\phi^p)\},$$

$$\mathcal{G}_{H_0}(\phi) = \inf\{(f, H_0 f)_{L^2} | f \in W_N, f \mapsto (\rho_\phi, j_\phi^p)\}.$$

Note that, by Theorem 4 and Theorem 6, there exists a $\psi_m \in W_N$ and a $\phi_m \in W_S$ such that $\mathcal{G}_{H_0}(\phi) = (\psi_m, H_0 \psi_m)_{L^2}$ and $\mathcal{G}_K(\phi) = (\phi_m, K \phi_m)_{L^2}$ and where $\psi_m, \phi_m \mapsto (\rho_\phi, j_\phi^p)$. Furthermore, we can use the existence of the minimizers ψ_m and ϕ_m and define, for $\phi \in W_S$,

$$\Delta T(\phi) = (\psi_m, K \psi_m)_{L^2} - (\phi_m, K \phi_m)_{L^2},$$

$$E_{xc}^W(\phi) = (\psi_m, \sum_{1 \leq k < l \leq N} |x_k - x_l|^{-1} \psi_m)_{L^2} - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_\phi(x)\rho_\phi(y)}{|x-y|} dx dy.$$

On W_S , we now introduce the following energy functional

$$\begin{aligned} \mathcal{G}_{v,A}(\phi) &= (\phi, K \phi)_{L^2} + \Delta T(\phi) + 2 \int_{\mathbb{R}^3} j_\phi^p \cdot A \\ &\quad + \int_{\mathbb{R}^3} \rho_\phi(v + |A|^2) + E_{xc}^W(\phi) + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_\phi(x)\rho_\phi(y)}{|x-y|} dx dy. \end{aligned}$$

We then have

Theorem 7 Assume that $H(v, A)$ has a unique ground-state ψ_0 . Let $e_0(v, A)$, ρ_0 and j_0^p denote the ground-state energy, ground-state particle density and ground-state paramagnetic current density, respectively. If $N < 4$ we assume that $\nabla \times (j_0^p/\rho_0) = 0$. Then

$$e_0(v, A) = \inf\{\mathcal{G}_{v,A}(\phi) | \phi \in W_S\} = \mathcal{G}_{v,A}(\phi_m)$$

for some $\phi_m \in W_S$. Moreover, $\rho_{\phi_m} = \rho_0$ and $j_{\phi_m}^p = j_0^p$, i.e., the ground-state densities can be computed from the determinant ϕ_m that minimizes $\mathcal{G}_{v,A}$.

Proof. First note, for any $\phi \in W_S$, we have

$$\begin{aligned} \mathcal{G}_{v,A}(\phi) &= (\phi, K\phi)_{L^2} + ((\psi_m, K\psi_m)_{L^2} - (\phi_m, K\phi_m)_{L^2}) \\ &\quad + 2 \int_{\mathbb{R}^3} j_\phi^p \cdot A + \int_{\mathbb{R}^3} \rho_\phi(v + |A|^2) + (\psi_m, \sum_{1 \leq k < l \leq N} |x_k - x_l|^{-1} \psi_m)_{L^2} \\ &\geq (\psi_m, (K + \sum_{1 \leq k < l \leq N} |x_k - x_l|^{-1}) \psi_m)_{L^2} + 2 \int_{\mathbb{R}^3} j_\phi^p \cdot A + \int_{\mathbb{R}^3} \rho_\phi(v + |A|^2) \\ &= \mathcal{E}_{v,A}(\psi_m) \geq e_0(v, A), \end{aligned}$$

where we used that $(\phi, K\phi)_{L^2} - (\phi_m, K\phi_m)_{L^2} \geq 0$ and $\psi_m \mapsto (\rho_\phi, j_\phi^p)$. In the next step, we want to show that there exists a $\phi_0 \in W_S$ such that $\mathcal{G}_{v,A}(\phi_0) = e_0(v, A)$ and $\phi_0 \mapsto (\rho_0, j_0^p)$.

Let $\phi \in W_S$ be a determinant such that $\phi \mapsto (\rho_0, j_0^p)$ (if $N < 4$, we need the assumption $\nabla \times (j_0^p/\rho_0) = 0$). By Theorem 6, we then have

$$\mathcal{G}_K(\phi) = T_{\det}(\rho_0, j_0^p) = (\phi_m, K\phi_m)_{L^2},$$

for some $\phi_m \in W_S$. Note that ϕ_m is a determinant such that $\phi_m \mapsto (\rho_0, j_0^p)$ and

$$\mathcal{G}_K(\phi_m) = (\phi_{m,m}, K\phi_{m,m})_{L^2} = (\phi_m, K\phi_m)_{L^2}.$$

Furthermore,

$$\mathcal{G}_{H_0}(\phi_m) = Q(\rho_0, j_0^p) = (\psi_m, H_0\psi_m)_{L^2},$$

for some $\psi_m \in W_N$, which follows from Theorem 4. Note that $\psi_m \mapsto (\rho_0, j_0^p) = (\rho_{\phi_m}, j_{\phi_m}^p)$.

We have,

$$\begin{aligned} e_0(v, A) &= (\psi_m, H(v, A)\psi_m)_{L^2} \\ &= (\psi_m, H_0\psi_m)_{L^2} + 2 \int_{\mathbb{R}^3} j_0^p \cdot A + \int_{\mathbb{R}^3} \rho_0(v + |A|^2) \\ &= (\psi_m, K\psi_m)_{L^2} + (\psi_m, \sum_{1 \leq k < l \leq N} |x_k - x_l|^{-1} \psi_m)_{L^2} + 2 \int_{\mathbb{R}^3} j_{\phi_m}^p \cdot A + \int_{\mathbb{R}^3} \rho_{\phi_m}(v + |A|^2), \end{aligned}$$

where the first equality follows from Proposition 5. Since

$$\Delta T(\phi_m) = (\psi_m, K\psi_m)_{L^2} - (\phi_m, K\phi_m)_{L^2}$$

and

$$E_{xc}^W(\phi_m) = (\psi_m, \sum_{1 \leq k < l \leq N} |x_k - x_l|^{-1} \psi_m)_{L^2} - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\phi_m}(x) \rho_{\phi_m}(y)}{|x - y|} dx dy,$$

it follows that

$$\begin{aligned} e_0(v, A) &= (\phi_m, K\phi_m)_{L^2} + 2 \int_{\mathbb{R}^3} j_{\phi_m}^p \cdot A + \int_{\mathbb{R}^3} \rho_{\phi_m}(v + |A|^2) \\ &\quad + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho_{\phi_m}(x) \rho_{\phi_m}(y)}{|x - y|} dx dy + E_{xc}^W(\phi_m) + \Delta T(\phi_m) = \mathcal{G}_{v,A}(\phi_m). \blacksquare \end{aligned}$$

Remarks. (i) Any density pair (ρ, j^p) computed from a $\phi \in W_S$ is N -representable, but not necessarily (non-interacting) v -representable. So Theorem 7 establishes a Kohn-Sham approach for N -representable densities (whereas T_{KS} is only defined on \mathcal{A}'_N).

(ii) Recall that no Hohenberg-Kohn theorem can exist for CDFT formulated with the paramagnetic current density. On the other hand, since ρ and j^p determine the ground-state, the Hohenberg-Kohn variational principle continues to hold for CDFT formulated with these densities. However, the N -representable Kohn-Sham approach outlined here does not use any variational principle for densities. Instead, the approach relies on the existence of minimizers for certain functionals.

(iii) If we set $\phi(x_1, \dots, x_N) = (N!)^{-1/2} \det[f^k(x_l)]_{k,l}$ and define on $(\mathcal{H}^1(\mathbb{R}^3))^N$ the functional

$$\begin{aligned} \mathcal{E}(f^1, \dots, f^N) &= \sum_{k=1}^N \int_{\mathbb{R}^3} |\nabla f^k|^2 + 2 \sum_{k=1}^N \int_{\mathbb{R}^3} \text{Im}(\bar{f}^k \nabla f^k) \cdot A + \sum_{k=1}^N \int_{\mathbb{R}^3} |f^k|^2 (v + |A|^2) \\ &\quad + \frac{1}{2} \sum_{k,l=1}^N \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|f^k(x)|^2 |f^l(y)|^2}{|x - y|} dx dy + E_{xc}, \end{aligned}$$

where $E_{xc} = \Delta T + E_{xc}^W$, we can obtain the usual Kohn-Sham equations by minimizing $\mathcal{E}(f^1, \dots, f^N)$ subject to the constraint $(f^k, f^l)_{L^2} = \delta_{kl}$.

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